Formation of silicon oxide nanowires in nanomaterial synthesis experiments based on the usage of tube furnace

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In an effort to synthesize doped ZnO nanowires, SiOx nanowires were obtained accidently. In the experiment, mixed powders containing chemicals such as ZnO, graphite, Ga2O3, and In2O3 were placed in the center of a tube furnace, where the temperature was set to 1200 °C and the vacuum was approximately 27 Pa. Silicon wafers were placed around the vicinity of the furnace exit to collect the expected nanomaterials. After prolonged heating, grey layers were found on top of one wafer located inside the furnace. The layer showed no adhesion to the substrate. Characterization by using Scanning Electron Microscope (SEM), Transmission Electron Microscope (TEM), and Energy Dispersive X-ray Spectroscopy (EDS) revealed that this layer consisted of SiOx nanowires. Formation of Si-containing liquid drop and the subsequent growth of SiOx nanowires out of it are suggested as the growth mechanism.

Keywords: silicon; oxide; nanowires

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1. Introduction

Nanomaterials are attractive due to the dramatic change in their properties accompanying the reduction of size. Examples of such changes include the emission of light with different wavelengths due to the effect of quantum confinement [1], and the improved efficiency of catalyst in the shapes of nanoparticles due to increased surface area [2]. Nanomaterials made of substances widely used in the bulk form are more attractive since they can be integrated to existing technology relatively easily [3, 4]. One example is the fabrication of SiOx nanowires. In this paper, we define silicon oxide as SiOx, with x values ranging from 1 to 2. In the form of bulk, silicon oxide is widely used as a window material in construction and as an insulator in the semiconductor industry. It has been reported that such ordinary materials show novel properties when fabricated as nanomaterials such as SiOx nanowires displaying luminescence [5]. For these reasons, fabrication of SiOx nanowires draws the attention of many researchers.

There were several previous reports regarding the fabrication of SiOx nanowires which we would like to divide into two groups, depending on their suitability for mass production [6]. Examples of approaches unsuitable for mass production include laser ablation, rapid thermal annealing, and sol-gel approaches. Laser ablation without a catalyst was reported by Yu et al. [7]. A similar experiment was performed by Aharonovich with a catalyst added [8]. Lai et al. used rapid thermal annealing to synthesize SiOx nanowires [9]. Sood et al. obtained SiOx nanowires by annealing Si wafers doped with Pd at 1100 °C [10]. Liang et al. yielded SiOx nanowires based on the usage of sol-gel process [11]. Synthesis of SiOx based on the heating of Si or SiOx is considered to be suitable for mass production. Jiang et al. used Chemical Vapor Deposition (CVD) to obtain SiOx, where Fe–Co–Ni alloy was used as the catalyst and Si powder as the source [12]. A similar experiment was performed
by Yang et al. [13]. Saulig-Wengner et al. reported the direct formation of SiOₓ from commercial Si powder in the presence of graphite powder [14]. The importance of graphite presence and the subsequent formation of CO and CO₂ was pointed out. In a similar experiment, Li et al. confirmed the effectiveness of graphite source in promoting the formation of SiOₓ [15]. In addition to graphite, the importance of Au as catalyst was emphasized in this later report. The effectiveness of graphite in promoting the formation of SiOₓ nanowires was supported by the experiment of Pukird et al., where SiOₓ nanowires were synthesized from rice husks using coconut shells [16]. In the present paper, we report the formation of SiOₓ nanowires in a CVD experiment. This experiment was originally designed to fabricate In or Ga doped ZnO nanowires, but SiOₓ nanowires were created accidentally. The approach used here is different from any of those described above. The formation mechanism is discussed in relation with the above mentioned reports.

2. Experimental

A schematic drawing for the configuration of the synthesis experiment is shown in Fig. 1. The furnace used was 51.5 cm long with a ceramics tube of 1 m length and 52 mm inner diameter inserted inside of it. In the vacuum pump side (downstream), the ceramics tube projected 15 cm out of the furnace. Raw powders of ZnO, graphite, Ga₂O₃, and In₂O₃ in different weight ratios were mixed thoroughly by grinding for a duration of 30 minutes. In some of the experiments, In₂O₃ powder was not used. One gram of the pre-prepared powder was packed in a relatively small ceramics boat of dimensions 2.96 × 0.81 × 0.69 cm³. This small ceramics boat was, in turn, placed in the center of a larger boat. Two extra empty small boats were placed on both sides of powder-containing boat to hold it in position. The large boat was placed in the center of the furnace. Four or six Si wafers of 3 to 3.5 cm in length were placed in medium sized ceramics boats with dimensions 4.04 × 3.06 × 0.71 cm³. These boats were placed in the vicinity of the down stream furnace exit with equal numbers inside and outside of the exit. The original purpose of the Si wafer was to be used as the substrate for the synthesized doped ZnO nanomaterials. The ceramics tube was evacuated to a vacuum of 27 Pa. The temperature was raised from room temperature to 1200 °C in two hours. The furnace was held at this temperature for three hours, and then allowed to cool to room temperature naturally. While the temperature at the center of the tube furnace was maintained at 1200 °C, there was decreasing temperature gradient from the inner Si wafer to the outside one. Since melt glass layers were found occasionally on the surface of the innermost Si wafer, the temperature at this point is estimated to be around 1000 °C while the temperature at the location of wafers placed in the outmost location is estimated to be around 400 °C. Examination of the large and small ceramics boats after the experiment found leftover black graphite powder, implying that other source materials were completely exhausted. The SiOₓ nanowires were found on the surface of Si wafers placed inside the furnace. Such SiOₓ nanowires were examined by Scanning Electron Microscope (SEM) (JEOL JIB-4500 Multi Beam System) and Energy Dispersive X-ray Spectroscopy (EDS) (EDAX Genesis). Some of the samples were examined by Transmission Electron Microscopy (TEM) (JEOL JEM-2100).

3. Results and discussion

SiOₓ nanowires were found in a synthesis experiment with mixed raw powders of ZnO:C:Ga₂O₃:In₂O₃ with a weight ratio of 10:2:1:2 respectively. The surface morphology of the Si wafer, on which SiOₓ nanowires were found, is shown in Fig. 2. The whole wafer was covered with a layer of grey color. There is little adhesion between the SiOₓ layer and the substrate such that even normal breathing could separate them. The upper right corner shows the morphology when the layer is intact while the lower left corner shows the substrate when the layer was removed. A SEM image of the SiOₓ nanowire layer peeled off from the substrate is shown in Fig. 3(a). The layer showed strong charging effect, implying the insu-